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(54) Title: METHOD FOR CREATION OF CONTROLLED FIELD EMISSION SITES

(57) Abstract

A method for creating controlled field emission sites in the surface of carbon films or carbon-based materials is provided. A laser beam is used to impinge upon the surface at sites from which emssion is desired, the duration of exposure of each site adjusted to each site provides the desired emission intensity. Electron emitters made according to the invention are useful in flat panel displays and other applications using electron emitters.

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TITLE

METHOD FOR CREATION OF CONTROLLED FIELD EMISSION SITES

FIELD OF THE INVENTION

This invention generally relates to a method for creating controlled field emission sites in carbon-based materials and to the use of such materials in electronic applications such as display panels. In particular, the invention relates to having a laser beam impinge upon the surface of a carbon-based material at sites from which controllable emission is desired.

GOVERNMENT RIGHTS

This invention was made with Government support through contract DE-AC04-94AC8500 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

Field emission electron sources, often referred to as field emission materials or field emitters, can be used in a variety of electronic applications, e.g., vacuum electronic devices, flat panel computer and television displays, emission gate amplifiers, and klystrons.

Display panels are used in a wide variety of applications such as home and commercial large screen televisions, laptop and desktop computers, and indoor and outdoor advertising and information presentations. Flat panel displays are only a few inches thick in contrast to the deep cathode ray tube monitors found on most televisions and desktop computers. Flat panel displays are a necessity for laptop computers, but also provide advantages in weight and size for many of the other applications. Currently, laptop computer flat panel displays use liquid crystals which can be switched from a transparent state to an opaque one by the application of small electrical signals. However, it is difficult to reliably produce these displays in sizes larger than that suitable for laptop computers.

Plasma displays have been proposed as an alternative to liquid crystal displays. A plasma display uses tiny pixel cells of electrically charged gases to produce an image and requires relatively large electrical power to operate.

So-called flat panel displays (which can be flat or curved), having a cathode using a field emission electron source, i.e., a field emission material or field emitter, and a phosphor capable of emitting light upon bombardment by electrons emitted by the field emitter have been proposed. Such displays have the potential for providing the visual display advantages of the conventional cathode ray tube and the depth, weight and power consumption advantages of the other flat panel displays.

Cold cathode field emitters are materials that have low voltage spontaneous electron emission in a vacuum. Such field emitters have many potential benefits over conventional flat panel display technologies; these benefits include high brightness, high contrast and low power consumption. One promising material for use as a field emitter is hydrogen-free amorphous tetrahedral-coordinated carbon (hereinafter referred to as "a-tC"). A film of this material is usually grown in a hydrogen-free atmosphere using pulsed laser deposition to produce a carbon film with a significant portion of the carbon atoms in a diamond-like tetrahedral coordination. Such films have been shown to be excellent field emitters and do not require the high vacuums necessary with some other field emitters. Flat panel display emitters must be readily and reproducibly addressable and must exhibit the same intensity of emission from the various emission sites. A major problem with a-tC films and other field emitters is the difficulty in controlling the location and intensity of electron emission sites. The films tend to emit at random points in the film, with varying intensities and at varying threshold voltages.

As a result of the above, it is clear that there is a need for a method of producing emitters in which the emission sites are controllable and the emission characteristics uniform and reproducible. Other objects and advantages of the present invention will become apparent to those skilled in the art upon reference to the drawings and the detailed description of the invention which hereinafter follow.

SUMMARY OF THE INVENTION

This invention provides a method for producing controllable emission sites in carbon-based materials. As used herein, this includes, but is not limited to, carbon coatings, films, and fibers as well as other bulk carbon-based materials of varying size and shape. The carbon can be in various forms, e.g., a-tC carbon, graphite, diamond, diamond-like carbon or glassy carbon.

The method comprises having a laser beam impinge upon the surface of the carbon-based material at sites from which emission is desired. Preferably, the regions of the carbon-based material surface containing the desired emission sites are voltage biased while the laser beam impinges upon these sites, the emission monitored and the duration of the exposure of each site to the laser beam adjusted so that each site provides the desired emission intensity.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 shows a schematic view of a laser light being focused onto the surface of a carbon-based material.

FIGURE 2 shows an embodiment wherein a regular array of emission sites were generated by rastering a laser beam over the surface of a carbon-based material.

FIGURE 3 shows a Fowler-Nordheim plot of emission data for a excimer laser-treated graphite fiber according to the invention.

FIGURE 4 shows comparative Fowler-Nordheim plots of an untreated graphite fiber and laser-treated graphite fibers made according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention provides a method for constructing a practical field emission electron emitter utilizing a carbon film or carbon-based material surface for use in flat panel displays and other electronic applications using electron emitters.

The carbon film used in this method can be prepared by any process. Preferably, the carbon film is an a-tC film. Usually, the carbon film will be formed and used on a substrate. These carbon films can contain dopants such as hydrogen, nitrogen and silicon. The substrate material is not critical and can be chosen from such diverse materials as silicon and other semiconductors, glass and metals. The substrate can have the form suitable for the particular application and, for instance, may be planar or in the form of fibers.

Additionally, the direct modification of carbon-based materials, having no film coating, is also possible. In this method, the laser is focused directly onto the surface of a carbon-based material (e.g., flat surface or uncoated fiber surface) to stimulate the creation of controlled emission sites. For this case, a "carbon-based material" is defined more broadly to include any shape of bulk carbon material, such as a fiber.

The wavelength of the laser light impinging on the carbon film or carbon-based material surface should generally be from about 150 nm to about 1100 nm. Preferably, an excimer laser is used as the source of the laser light and the preferred range of wavelength of the light is accordingly from about 193 nm to about 248 nm. When a carbon film is used, the amount of energy absorbed by the carbon film in the area of the desired emission site must be sufficient to modify the structure of the carbon at that site but not so large as to substantially ablate the carbon film from the substrate. Typically, energy densities of from about 0.01 J/cm^2 to about 45 J/cm^2 and power densities of from

about $5x10^6$ W/cm^2 to about $5x10^9$ W/cm^2 are used. Suitable excimer lasers usable in the inventive method include a LPX 300 or EMG 150 commercially available from Lambda Physik of Acton, MA.

Emission can be initiated or enhanced at programed positions in the surface of the carbon film or carbon-based material by rastering the laser over the surface and allowing the laser beam to impinge the surface and create the desired emission sites only at the pre-determined programed sites. Emission sites could thus be created over the whole surface, along linear paths in the surface, at regularly spaced areas to produce pixels, or in any other configuration deemed desirable.

Treatment with the laser beam can be accomplished following production of the carbon film or carbon-based material or during the assembly of an electronic device or display using the carbon film or carbon-based material emitter.

The laser beam can impinge upon the carbon film or carbon-based material in air, in vacuum, or in a partial pressure of gas spanning the range from ultra high vacuum to atmospheric pressure. Preferably, the atmosphere contains gases such as hydrogen and nitrogen to stabilize and enhance the emission properties.

During the time the laser beam impinges a desired emission site, that region of the carbon film or carbon-based material surface can preferably be voltage biased so that emission from the site can be monitored and the duration of the exposure of that site to the laser beam can be adjusted. In this way, the laser beam treatment can be varied to insure that each site provides the desired emission intensity. Each site can be exposed so that they all provide the identical emission intensity or so that the intensity is varied from site to site according to a desired and pre-determined pattern.

FIG. 1 shows a simple schematic of a laser light being focused onto the surface of a carbon film or carbon-based material according to one embodiment of the

invention. FIG. 2 shows an example wherein a regular array of emission sites were generated by rastering a laser beam over the surface of a carbon film or carbon-based material.

EXAMPLES

The following non-limiting examples are intended to further demonstrate the inventive method and the field emission electron emitters resulting therefrom.

EXAMPLE 1

The surface of an untreated graphite fiber (commercially available IM7 graphite fiber from Hercules, Inc., Wilmington, DE) was exposed to an excimer laser (EMG 150, Lambda Physik, Acton, MA). The energy density was about 0.5 J/cm^2. The emission current for the resulting laser-treated fiber is shown in Figure 3 on a Fowler-Nordheim plot. The resultant fiber was shown to be an excellent field emitter.

EXAMPLE 2

A comparison was made between the emissive properties of an untreated graphite fiber and those of laser-treated graphite fibers in a vacuum and laser-treated graphite fibers in a hydrogen atmosphere. The laser-treated graphite fibers were prepared according to the inventive method. Fowler-Nordheim plots were prepared for each of the three (3) samples in FIG. 4. The laser-treated graphite fibers show enhanced emissive properties over the untreated graphite fibers.

Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous modifications, substitutions and rearrangements without departing from the spirit or essential attributes of the invention. Reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

WHAT IS CLAIMED IS:

1. A method for creating controlled field emission sites in carbon-based material surfaces, the method comprising exposing the surface of a carbon-based material to a laser beam such that the beam impinges upon the surface at sites from which emission is desired, wherein the amount of energy absorbed by the surface in the area of the desired emission site is sufficient to modify the structure of the carbon at that site but not so large as to substantially ablate the surface.

2. The method of Claim 1 wherein the carbon-based material is an a-tC film.

3. The method of Claim 2 wherein the a-tC film is supported on a substrate during laser beam exposure.

4. The method of Claim 3 wherein the substrate is fabricated from a material selected from the group consisting of silicon, glass and metal.

5. The method of Claim 3 wherein the substrate is planar.

6. The method of Claim 3 wherein the substrate is a fiber.

7. The method of Claim 1 wherein the wavelength of the laser beam is between about 150 nm to about 1100 nm.

8. The method of Claim 1 wherein the energy density used in the area of the desired emission site is between about 0.01 J/cm^2 and about 45 J/cm^2.

9. The method of Claim 1 wherein the power density used in the area of the desired emission site is between about $5x10^6$ W/cm^2 and about $5x10^9$ W/cm^2.

10. The method of Claim 1 wherein the carbon-based material is a graphite fiber.

11. A field emission electron emitter produced by the method of Claim 1.

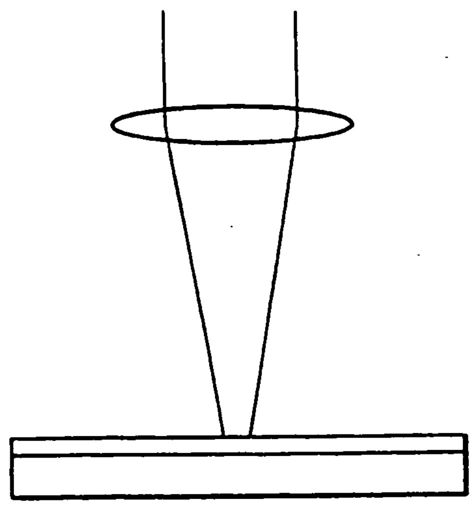


FIG.1

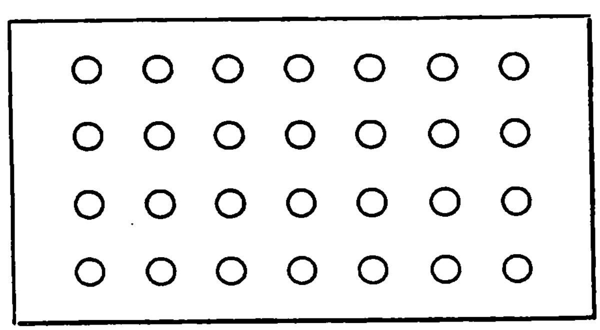
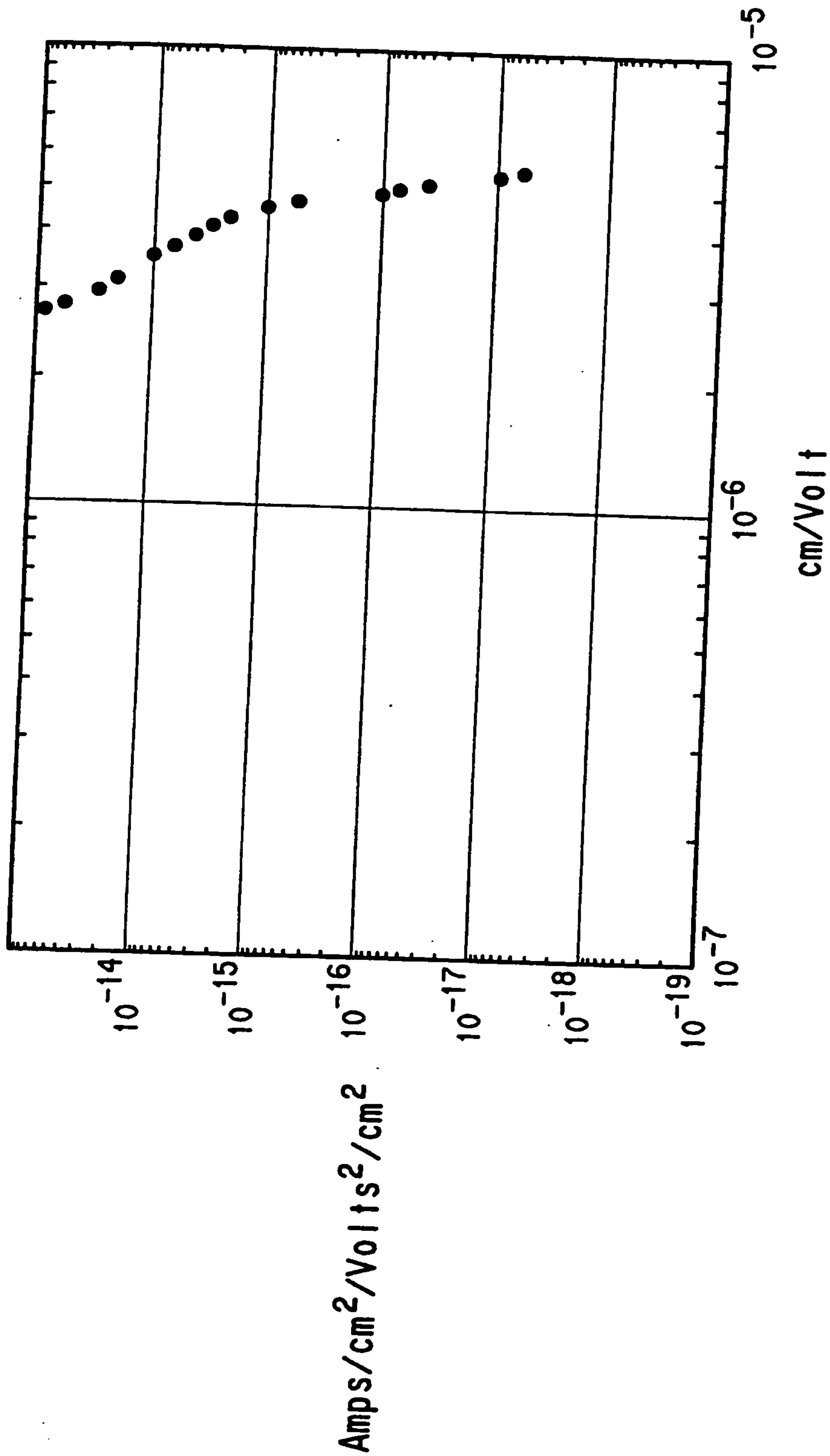


FIG.2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10^{-7}
cm/Volt
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10^{-16}
10^{-17}
10^{-18}
10^{-19}
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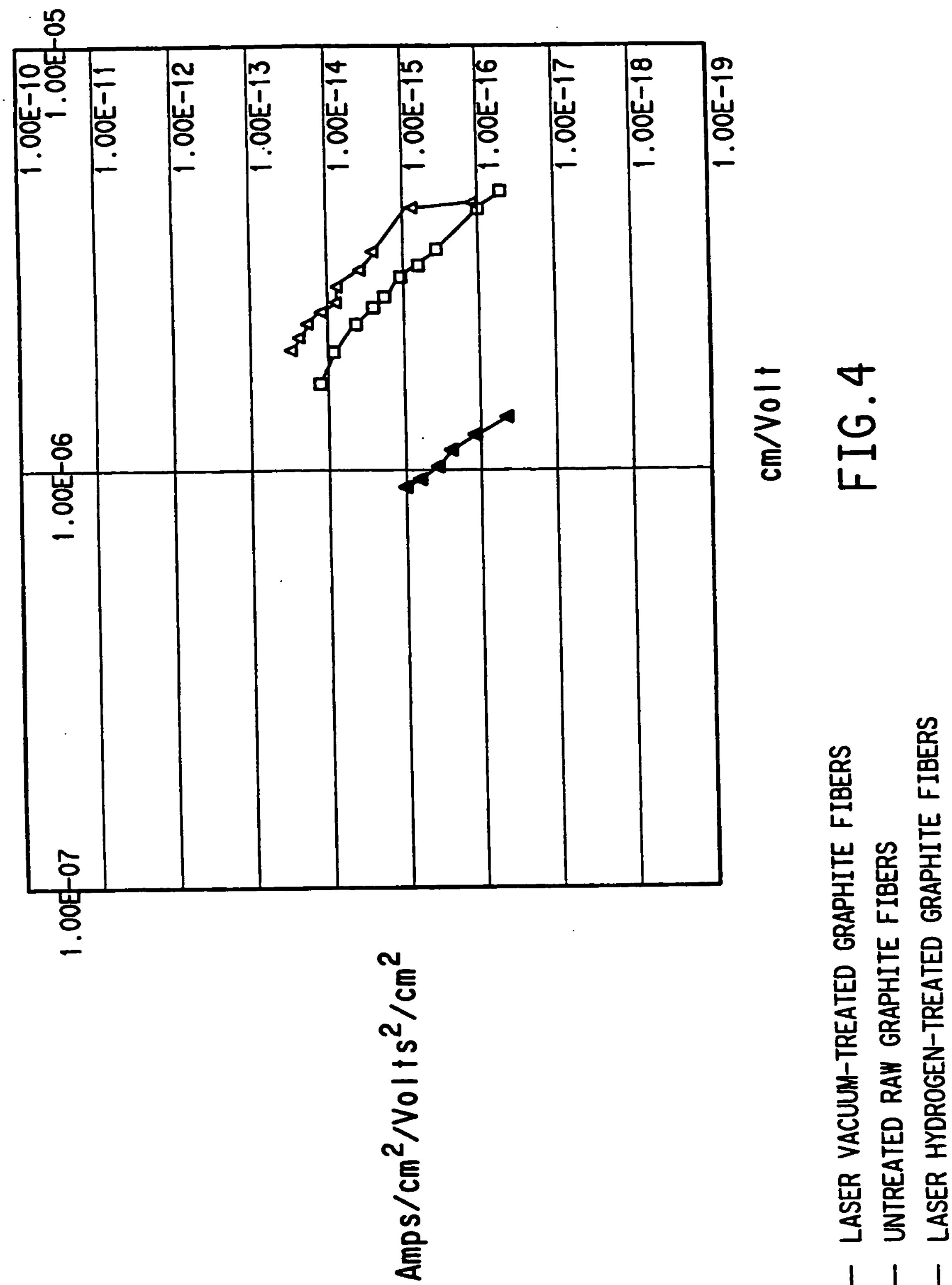
FIG. 3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1.00E-15
1.00E-16
1.00E-17
1.00E-18
1.00E-19
cm/Volt
Amps/cm²/Volts²/cm²
LASER VACUUM-TREATED GRAPHITE FIBERS
UNTREATED RAW GRAPHITE FIBERS
LASER HYDROGEN-TREATED GRAPHITE FIBERS

FIG. 4

INTERNATIONAL SEARCH REPORT

Inter   nal Application No
PCT/US 96/12824

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01J9/02 H01J1/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,96 00974 (SILICON VIDEO CORP ;MASSACHUSETTS INST TECHNOLOGY (US); ADVANCED T) 11 January 1996 see page 18, line 2-6; claims 19-21 ---	1
Y	EP,A,0 609 532 (MOTOROLA INC) 10 August 1994 see column 4, line 20 - column 8, line 54; claims 1-7 ---	1-5,7-9, 11
Y	APPLIED PHYSICS, vol. a, no. 58, 1994, pages 137-144, XP000608573 L.C.NISTOR ET AL.: "direct observation of laser-induced crystallization of a- C:H FILMS" see page 137 - page 144 ---	1-5,7-9, 11

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[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 November 1996	13. 11. 96
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Inte   nal Application No
PC1/US 96/12824

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

nformation on patent family members

Int ional Application No
PCT/US 96/12824

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